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Final Project Report:

NITROGEN RINGS AND CAGES STABILIZED BY METALLIC ATOMS

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Summary of activities

Over the last four years, our research has been focused on the prediction of new molecular species. The initial aim of this project was to study on paper new nitrogen compounds that were stabilized by metal centers. We did not find any new attractive nitrogen species. However, the algorithms developed during this project are universal and allow us to study other interesting chemical systems like silicon-lithium clusters. Particularly, we developed two new techniques, the first one is a new way to calculate a Fukui function, the second one is a genetic algorithm to search for global minimum species. This AFOSR project funded directly three publications in some of the most important journals in the chemical community, such as J. Am. Chem. Soc., J. Chem. Phys., and Organometallics. Two more manuscripts are in progress. On the other hand, two postdoc positions were financed by this project.

The projects funded by AFOSR were:

- 1) *Structure and Bonding of $[E-Cp-E']^+$ Complexes (E and $E' = B-Tl$; $Cp =$ Cyclopentadienyl)*

Our first attempt to study the $Al-\eta^5-N_5$ complex failed. However, we found an interesting family of compounds with formula $[E-Cp-E']$, which structure was close to that suggested by the $Al-\eta^5-N_5$ complex. The geometries and metal–ligand bond dissociation energies of $[E-Cp-E']^+$ complexes ($E, E' =$ group 13 element; $Cp =$ cyclopentadienyl) were calculated within the density functional theory framework. The geometries of the title complexes were optimized at the BP86 level with the TZ2P valence basis set. The nature of the metal–ligand bonding has been studied using the energy decomposition analysis (EDA). The calculated bond strengths for the homoleptic complexes $[E-Cp-E]^+$ with respect to loss of a neutral or charged group 13 atom are $Ga > Al > In > Tl > B$. While the energetically most favorable pathway for the boron complex $[B-Cp-B]^+$ is the loss of a neutral boron atom, heavier homologues $[E-Cp-E]^+$ ($E = Al-Tl$) dissociate via loss of the charged atom E^+ . The heteroleptic species $[E-Cp-E']^+$ are less stable than the homoleptic complexes $[E-Cp-E]^+$. The lowest energy pathway for dissociation is the loss of the positively charged heavier atom E^+ . The B-Cp interactions in the boron complexes

have a larger (covalent) orbital character than the E-Cp bonding in the heavier homologues. The energy decomposition analysis of $[\text{E-Cp-E}]^+$, using Cp^- and $(\text{E}\cdots\text{E})^{2+}$ as ligands, suggests that the $a_1(\sigma)$ bonding has nearly the same strength as the $e_1(\pi)$ bonding. This study was published in *Organometallics* (Fernandez, I.; Cerpa, E.; Merino, G.; Frenking, G. *Organometallics* **2008**, 27, 1106-1111.).

2) *Efficient Evaluation of Analytic Fukui Functions*

An efficient method for the analytic evaluation of Fukui functions was proposed. Working equations were derived and numerical results were used to validate the method on medium size set of molecules. In addition to the obvious advantages of analytic differentiation, the proposed method is efficient enough to be considered a practical alternative to the finite difference formulation used routinely. Particularly, some problems found in other methods for prediction of electrophilic centers are corrected automatically when using the new method. This algorithm was programmed in deMon-2k. This study was published in the *Journal of Chemical Physics*. (Flores-Moreno, R.; Melin, J.; Ortiz, J. V.; Merino, G. *J. Chem. Phys.* **2008**, 129, 224105-224111.)

3) *Designing a three-dimensional molecular star*

We have explored in detail the potential energy surfaces of the $\text{Si}_5\text{Li}_n^{5-n}$ ($n = 5-7$) systems. We found that it is feasible to design three-dimensional star-like silicon structures using the appropriate ligands. The global minimum structure for Si_5Li_7^+ has a perfect seven-peak star-like structure. These compounds comprise, essentially, the Si_5^{6-} ring interacting with lithium cations. The ionic character of the Si-Li interactions induces the formation of a bridged structure. Concomitantly, our calculations show that the reduction of the Pauli repulsion and the maximization of the orbital contribution are also significant for the star-like structure formation. Additionally, the MO analysis of the systems suggests that the role of the lithium atoms is to provide the precise number of electrons to the central Si_5 unit. This is confirmed by the magnetic properties, which show that electron delocalization enhances the stability of the star-like structures. This manuscript was published in

the Journal of the American Chemical Society (Tiznado, W.; Perez-Peralta, N.; Islas, R.; Toro-Labbe, A.; Ugalde, J. M.; Merino, G. *J. Am. Chem. Soc.*, **2009**, *131*, 9426–9431.

- 4) Two more projects are in progress. The first one is the stabilization of carbon-aluminum cluster with a star-like structure. This work has been submitted to Chemical Communications for its publications. The second one is the development of Quaerere. This program is a genetic algorithm for searching a global minimum structure. Quaerere has an interface with Gaussian, ADF, and deMon. Quaerere includes more genetic operation than other similar programs like GEGA.

Publications

1. Fernandez, I.; Cerpa, E.; **Merino, G.***; Frenking, G. Structure and Bonding of $[E-Cp-E']^+$ complexes (E and E' = B–Ti; Cp = Cyclopentadienyl). *Organometallics* **2008**, *27*, 1106-1111.
2. Flores-Moreno, R.; Melin, J.; Ortiz, J. V.; **Merino, G.** Efficient Evaluation of Analytic Fukui Functions. *J. Chem. Phys.* **2008**, *129*, 224105-224111.
3. Tiznado, W.; Perez-Peralta, N.; Islas, R.; Toro-Labbe, A.; Ugalde, J. M.; **Merino, G***. Designing 3-D molecular stars. *J. Am. Chem. Soc.*, **2009**, *131*, 9426–9431.
4. Wu, Y.; Jiang, J.-L.; Lu, H.; Wang, Z.; Perez-Peralta, N.; Islas, R.; **Merino, G.*** $C_5Al_5^-$: A Promising Anionic Molecular Star. **2009**, *Submitted*.

More than 25 manuscripts were published from 2006 to 2009 in some of the most important journal in the chemical community. Clearly, the AFOSR project helps to consolidate the theoretical group in the Universidad de Guanajuato. Right now, our group is a world leader in the prediction of new molecular species.

Personal supported

Faculty

- Prof. Gabriel Merino

- Prof. Manuel Villanueva

Professional staff

- Dr. Francisco Tenorio
- Dr. Oscar Jimenez-Halla

Undergraduate students:

- America Bravo
- Kristel García
- Cristina Santiago

Again, the AFOSR project was a milestone to consolidate the group. Right now in our group there are ten Ph. D. and three undergraduate students. Our group is one of the most productive in Mexico and Latin-America in Theoretical Chemistry.

Honors and awards

Gabriel Merino was designed member of the national system of researchers with level 2 (the maximum level is 3)

Best undergraduate thesis in Chemistry in Mexico. Rafael Islas.